

## Description

### ALUMINIUM-WETTABLE CARBON-BASED BODY

#### Field of the Invention

- [1] The invention relates a carbon-based body having an aluminium-wettable surface. The body can be used as a component of an apparatus which during use contains molten aluminium that comes into contact with the component, for example an aluminium electrowinning cell or an apparatus for treating molten aluminium.

[2] **Background of the Invention**

- [3] The production, purification or recycling of aluminium is usually carried out at high temperature in very aggressive environments, in particular in molten aluminium, molten electrolyte and/or corrosive gas. Therefore, the materials used for the manufacture of components exposed to such environments must be thermally and chemically stable.
- [4] Graphite and other carbonaceous materials are commonly used for components, especially conductive components. Unfortunately, carbon components do not resist oxidation and/or corrosion and must be periodically replaced.
- [5] Several proposals have been made to reduce wear of carbon components in such technologies to achieve a higher operation efficiency, reduce pollution and the costs of operation.
- [6] For the purification of molten metals, in particular molten aluminium, by the injection of a flux removing impurities towards the surface of the molten metal, it has been proposed to coat carbon components which are exposed to the molten metal with a coating of refractory material as disclosed in WO00/63630 (Holz/Duruz), WO01/42168 (de Nora/Duruz), WO01/42531 (Nguyen/Duruz/de Nora) and WO02/096831 (Nguyen/de Nora).
- [7] In aluminium production, some components are exposed to molten fluoride-containing electrolyte, molten aluminium and/or anodically produced oxygen. In conventional Hall-Héroult cells these components are still made of consumable carbonaceous materials.
- [8] US Patents 5,378,327, 5,578,174 and 5,679,224 disclose increasing the resistance of carbon components used in aluminium electrowinning cells by impregnating the carbon with colloidal alumina, ceria, cerium acetate, lithia, silica, yttria, thoria, zirconia, magnesia or monoaluminium phosphate that contain species of sodium, lithium, potassium, aluminium, calcium or ammonium; or with a solution, suspension or melt of lithium, sodium or potassium.
- [9] The use of titanium diboride and other RHM current-conducting elements to protect or replace carbon components in electrolytic aluminium production cells is

described in US Patents 2,915,442, 3,028,324, 3,156,639, 3,215,615, 3,274,093, 3,314,876, 3,330,756, 3,400,061, 3,661,736, 4,093,524, 4,308,114, 4,466,996, 5,217,583, 5,310,476, 5,316,718, 5,364,513, 5,374,342, 5,618,403, 5,651,874, 5,728,466, 5,746,895 and 6,436,250.

[10] Recently, the aluminium-wettability of RHM coatings has been significantly improved by the addition of aluminium-reactable metal oxides, such as iron, copper, cobalt, nickel, zinc and manganese oxides, as disclosed in WO01/42168 (de Nora/Duruz), WO01/42531, (Nguyen/Duruz/ de Nora), WO02/096830 (Duruz/Nguyen/de Nora) and WO02/096831 (Nguyen/de Nora).

[11] Such RHM coated bodies have the following attributes: excellent wettability by molten aluminium, resistance to attack by molten aluminium and cryolite, low cost, environmentally safe, ability to absorb thermal and mechanical shocks, durability in the environment of an aluminium production cell, and ease of production and processing.

[12] **Summary of the Invention**

[13] An object of the invention is to provide a carbon body that is easy to manufacture and that has an aluminium-wettable surface.

[14] A main object of the invention is to provide a carbon body that has the desired mechanical, physical, chemical, and electrochemical characteristics so that it can be used in a molten aluminium environment, in particular in an aluminium electrowinning cell or in an apparatus for treating molten aluminium.

[15] The invention relates to a carbon body having an aluminium-wettable outer part that is made of a carbon-rich mixture containing metal-based particles and carbon. The metal-based particles are made of metal oxide particles and/or partly oxidised metal particles or a precursor thereof. The metal of the metal-based particles are selected from iron, copper, cobalt, nickel, zinc and manganese and combinations thereof. The metal oxide particles and/or partly oxidised metal particles are reactable with molten aluminium when exposed thereto to form a mixture of: aluminium oxide; the metal of said metal-based particles; and aluminium.

[16] Carbon is an aluminium-repellent material. However, it has been found that when carbon material is mixed with an aluminium-reactable metal oxide and/or partly oxidised metal, molten aluminium reacts therewith to form alumina and the metal derived from the metal oxide and/or partly oxidised metal by transfer of oxygen from the metal oxide and/or partly oxidised metal to the aluminium. The metal derived from the metal oxide and/or partly oxidised metal may then be alloyed with unreacted molten aluminium. Hence, the presence of the aluminium-reactable metal oxide and/or partly oxidised metal promotes infiltration of aluminium by reaction therewith into the carbon material.

[17] Moreover, alumina, aluminium and the metal derived from the metal oxide and/or

partly oxidised metal form a mixture that remains within the carbon material, in particular at its surface, and maintains it wetted by aluminium after reaction.

- [18] It has surprisingly been observed that the carbon body with the aluminium-wettable outer part according to the invention is less exposed to corrosion and erosion by molten aluminium compared to a non-wettable carbon body, despite penetration of aluminium into the body's outer part.
- [19] Without being bound to any theory, it is believed that the reduced corrodability and erodability of the carbon body according to the invention has two causes. On the one hand, the mixture of alumina, aluminium and the metal derived from the metal oxide and/or partly oxidised metal, formed at the body's outer part is less reactive than pure aluminium. Hence carbon reacts less with this mixture than it does with pure aluminium to form aluminium carbide. On the other hand, the aluminium layer that continuously wets the body's outer part during use inhibits exposure to the environment, e.g. cryolite, of the formed aluminium carbide and dissolution thereof into the environment.
- [20] The carbon body can be a fully manufactured body or a part-manufactured body that is subsequently, for example, subjected to a consolidation or conditioning treatment, e.g. a heat and/or aluminisation treatment.
- [21] The carbon-rich mixture is made predominantly of carbon, i.e. carbon is the mixture's main constituent.
- [22] The body can comprise an inner part that is substantially free of metal-based particles, the body's outer part having a thickness of 5 to 50 mm, in particular from 10 to 25 mm. Alternatively, the body comprises metal-based particles throughout.
- [23] In one embodiment, the metal-based particles are impregnated into the carbon body. In this case, the particles will be found in the body's pores, especially towards the body's surface. Typically, the carbon and the metal-based particles in the outer part are present in a weight ratio metal-based particles/carbon from 1/100 to 1/20, in particular from 1/50 to 1/25.
- [24] In another embodiment, the body's outer part is made of a heat treated mixture of the metal-based particles and particles of carbon. For example, the metal-based particles of the outer part are present in a weight ratio metal-based particles/carbon from 1/20 to 1/2, in particular from 1/8 to 1/4.
- [25] The outer part of the carbon body may comprise further particles of at least one additional metal compound. The additional metal compound(s) can be selected from refractory borides, silicides, nitrides, carbides, phosphides, oxides, aluminides, metal alloys, intermetallics, and mixtures thereof, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum and molybdenum. Usually, the further particles and the metal-based particles of the outer part are present in a weight ratio further

particles/metal-based particles from 1/10 to 1/2.

- [26] The metal-based particles can be present in the body's outer part in an organic carrier, in particular selected from pitch, polyurethane, ethylene glycol, polyethylene glycol, resins, esters or waxes, and/or an inorganic carrier, in particular selected from colloidal and/or polymeric metal compounds of metals selected from aluminium, silicon, yttrium, cerium, thorium, zirconium, tin, nickel, iron, chromium and magnesium which compounds form a metal oxide binder upon heat treatment.
- [27] The body can also be coated with an aluminium-wettable top coating which is free or substantially free of carbon. Examples of top coatings, in particular containing refractory borides and/or aluminium-reactable metal oxides, are disclosed in WO01/42168 (de Nora/Duruz), WO01/42531, (Nguyen/Duruz/de Nora), WO02/096830 (Duruz/Nguyen/de Nora) and WO02/096831 (Nguyen/de Nora).
- [28] The invention also relates to a carbon body having an aluminium-wetted outer part producible by exposing the above described body to molten aluminium. The outer part comprises a carbon-rich mixture containing: aluminium oxide; the metal of said metal-based particles; and aluminium.
- [29] The invention further relates to a method of manufacturing a carbon body. The method comprises providing a mass of carbon and the above aluminium-reactable metal-based particles; adding the metal-based particles into the mass of carbon so as to form a carbon-rich mixture containing the metal-based particles; and consolidating by heat treatment the metal-based particles in the carbon mass to form an aluminium-wettable outer part of the carbon body which outer part is made of a carbon-rich mixture containing the metal-based particles.
- [30] As mentioned above, the metal-based particles can be impregnated into the outer part of the carbon body that forms the carbon mass. The metal-based particles are then consolidated in the carbon body's outer part by heat treatment. Usually, the metal-based particles are introduced into the body's outer part with the aid of a liquid carrier. Typically, a solution, a dispersion or possibly a suspension will be used for the infiltration. The liquid carrier may be organic or inorganic, in particular aqueous. The metal-based particles in the carrier can be in ionic form (typical particle size below 5 nm), polymeric form (typical particle size from 5 to 10 nm) or colloidal form (typical particle size from 10 to 100 nm). The metal-based particles may be present in the liquid carrier in the form of an oxide or oxidised metal, or a precursor thereof such as a metal, nitride, chloride, hydroxide or a metal organic compound such as an alkoxide, a formate or an acetates. This precursor will usually turn into an oxide or surface oxidised metal upon heat-treatment.
- [31] The size of the metal-based particles used for the impregnation is sufficiently small that the metal-based particles can infiltrate the porosity of the carbon body. The metal-

based particles can be dissolved in a solution, or can be in polymeric or colloidal form in a liquid carrier and have a typical size below about 100 nm as mentioned above. When a high porosity carbon material is used, the metal-based particles may be suspended or slurried in a liquid carrier and can have a larger size, typically up to 1, 10, 30, 50 or 100 micron depending on the size of the pores.

- [32] Alternatively, the metal-based particles are mixed with carbon particles that form the carbon mass, the mixed carbon particles and metal-based particles being then consolidated by heat treatment to form the outer part of the carbon body. When the metal-based particles are mixed with the carbon particles, they may be in the form of an oxide or a surface oxidised metal, or a precursor thereof such as a metal, nitride, boride, carbide or metal organic compound. This precursor will usually turn into an oxide or surface oxidised metal upon heat-treatment.
- [33] For instance, a layer of the carbon particles and the metal-based particles can be consolidated on a substrate. The substrate can be either baked, or non-baked or part-baked in which case the layer and the carbon substrate can be consolidated together by heat treatment. For example, the layer of the particle mixture can be formed by co-extrusion followed by heat treatment.
- [34] Alternatively, the carbon particles and the metal-based particles can be consolidated to form a self-sustaining body.
- [35] The heat treatment can be carried out at a temperature above 200°-450°C and usually below 3000°C. Typically, consolidation of the particle mixture takes place at a temperature from about 250° to 650°C. However, the heat treatment can also take place at temperatures up to around 2000° to 3000°C, especially when a carbon green, e.g. a substrate, is consolidated at the same time.
- [36] When the metal-based particles are mixed with carbon particles and then consolidated, the metal-based particles may have any of the above sizes.
- [37] The above-mentioned further particles of at least one additional metal compound may be added into the mass of carbon.
- [38] Furthermore, the aluminium-wettable outer part can be exposed before or during use to molten aluminium to react the outer part's metal-based particles with molten aluminium and wet the outer part by aluminium.
- [39] Another aspect of the invention relates to a carbon-rich particle mixture for forming upon heat treatment a self-sustaining body or a layer of carbon that contains the metal oxide and/or partly oxidised metal. The particle mixture comprises carbon particles and the above described metal-based particles.
- [40] A further aspect of the invention relates to a component of an apparatus that during use contains molten aluminium. The component comprises a body with an outer part containing the metal-based particles as described above.

- [41] Yet another aspect of the invention relates to an apparatus that during use contains molten aluminium and comprises the above component.
- [42] This apparatus can be a cell for the electrowinning of aluminium, the above-mentioned component being a cathodic component, a cell bottom component or a sidewall component. Examples of aluminium electrowinning cells are for example disclosed in US Patents 5,683,559, 5,888,360, 6,093,304 (all de Nora), 6,358,393 and 6,436,273 (both de Nora/Duruz). Further cells are disclosed in PCT applications WO99/02764 (de Nora/Duruz), WO00/40781, WO00/40782 (both de Nora), WO00/63463 (de Nora), WO01/31086 (de Nora/Duruz), WO01/31088, WO02/070783, WO02/070785, WO02/097168 and WO02/097169 (all de Nora).
- [43] The apparatus may be an apparatus for treating molten aluminium, the above component being exposed during use to molten aluminium. Examples of such apparatus are disclosed in the abovementioned WO00/63630, WO01/42168, WO01/42531 and WO02/096831 .
- [44] Yet a further aspect of the invention relates to a method of operating the above apparatus. During operation the component is exposed to molten aluminium. When the apparatus is an aluminium electrowinning cell, the method comprises electrowinning aluminium which comes into contact with the component. When the apparatus is an apparatus for treating molten aluminium, the method comprises treating molten aluminium which comes into contact with the component.
- [45] **Detailed Description**
- [46] The invention will be further described in the following examples.
- [47] **Example 1**
- [48] A graphitized carbon block was made aluminium-wettable by impregnation with an iron compound and then the block was aluminised as follows.
- [49] An impregnation solution was prepared by mixing an amount of 100 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 50 g  $\text{H}_2\text{O}$  (density 1.4 g/cm<sup>3</sup>). The carbon block was impregnated by dipping into this solution at room temperature for 10 to 15 min. The carbon block was dried for 24 hours in air at 60 to 80°C and then heat treated in air between 250° and 500°C. During the heat treatment, the  $\text{Fe}(\text{NO}_3)_3$  was transformed into iron oxide and the block's colour turned red-brown (indicating the presence of  $\text{Fe}_2\text{O}_3$ ).
- [50] The block was impregnated over a depth of about 2.5 to 3 cm. The impregnated part of the carbon block contained about 1.5 weight%  $\text{Fe}_2\text{O}_3$ .
- [51] The impregnated carbon block was then dipped into a bath of molten aluminium at a temperature of 940°C. After 12 hours the carbon block was extracted from the molten aluminium. The block was wetted by an adherent thin layer of molten aluminium. Aluminium had impregnated the block's entire surface over a depth of at least 0.2 mm and locally up to about 20 mm and had partly alloyed with iron upon

reaction of aluminium and the block's iron oxide (forming alumina and iron metal that will usually alloy with aluminium).

[52]       **Example 2**

[53]       An aluminised graphitized carbon cathode block was prepared by the method of Example 1.

[54]       The aluminised block was then tested in a laboratory aluminium electrowinning cell containing an electrolyte made of 11 wt% aluminium fluoride ( $\text{AlF}_3$ ), 9.6 wt% alumina ( $\text{Al}_2\text{O}_3$ ), 5 wt% potassium fluoride (KF), 4 wt%  $\text{CaF}_2$ , the balance being cryolite ( $\text{Na}_3\text{AlF}_6$ ). An electrolysis current was passed through the block at a cathode current density of about 0.5 A/cm<sup>2</sup>.

[55]       After 80 hours, the electrolysis was interrupted and the cathode block examined. The block was still perfectly wetted by a film of molten aluminium. The penetration of the block by molten aluminium did not significantly change during operation in the cell.

[56]       **Example 3**

[57]       An aluminium-wettable carbon-based body was prepared and aluminised as follows.

[58]       A mixture of iron oxide and carbon was prepared by mixing 18 g of graphite powder (with a particle size below about 100 to 200 micron), 3 g iron oxide powder (with a particle size below about 45 micron) and 12 g pitch.

[59]       The mixture was cast into a plastic mould and allowed to dry for 12 hours to form a carbon-based block that was then heat treated for 2 hours at 450°C for consolidation.

[60]       After heat treatment, the carbon-based block was dipped into a bath of molten aluminium at a temperature of 940°C. After 12 hours the carbon block was extracted from the molten aluminium. The block was wetted by an adherent thin layer of molten aluminium and impregnated to a depth of about 0.2 mm by aluminium that had reacted and alloyed with iron upon reaction of aluminium and the block's iron oxide.

[61]       **Example 4**

[62]       An aluminised carbon-based body manufactured as in Example 3 was used as a cathode in a laboratory cell as in Example 2 and behaved similarly.

[63]       **Example 5**

[64]       A graphitized porous carbon block was made aluminium-wettable by impregnation with an iron compound and then the block was aluminised as follows.

[65]       An amount of 50 g of an aqueous solution containing colloidal iron hydroxide in a concentration equivalent to 55 wt% (27.5 g)  $\text{Fe}_2\text{O}_3$  (Timbasol WF Transparent Red - N10WL52 - JOHNSON MATHEY) was diluted in 50 g water. This diluted colloidal solution was used to impregnate the block by dipping it into the solution for 30 minutes. The carbon block was dried in air for 24 hours at 80°C and heat treated in air

at 450°C for 4 hours. During the heat treatment, the water of the impregnation was evaporated and the iron hydroxide turned mainly into black  $\text{Fe}_2\text{O}_3$ .

[66] The carbon block was covered with a layer of colloidal  $\text{Fe}_2\text{O}_3$  particles as well as impregnated over a depth of 3-4 cm from the block's surface. The impregnated part of the carbon block contained about 3 to 4 weight%  $\text{Fe}_2\text{O}_3$ .

[67] This colloidal impregnation was about 1 cm deeper than the  $\text{Fe}(\text{NO}_3)_3$  (dissolved) impregnation of Example 1 due to the low viscosity of the colloidal solution compared to the nitrate solution used in Example 1.

[68] The impregnated carbon block was aluminised as in Example 1.

[69] **Example 6**

[70] An aluminised graphitized carbon cathode block was prepared as in Example 1 and tested in a cell under the conditions described in Example 2.

[71] After 300 hours, the test was interrupted and the cathode block examined. No measurable wear or corrosion was observed on the cathode.

[72] In comparison, an untreated carbon block, i.e. non-impregnated and non-aluminised, used in a cell under the same conditions has wear rate of 1 mm per 100 hours.